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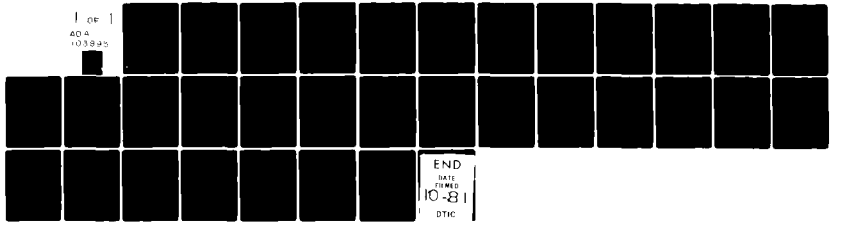

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Analyses for Mechanical Stability for Systems of Ions and Atoms Associated with Rings, Cages, and Crypts.

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There exist examples of systems in which small, simple metallic cations are associated with ring-like molecules (e.g., aromatic radical anions), with aggregates of molecules which encage the ion (e.g., solvation and coordination), or special molecules which trap ions within the molecular structure (crypts). For each of these examples, the harmonic oscillations of the ion in the presence of the molecular structure can be

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observed. Moreover, in many instances, the stability of the ionic motions in the presence of the molecular structure is important in considering some form of transport process which is associated with the ion. In this paper we present an analysis of the mechanics of the motion of an ion under the influence of various molecular structures. For our analyses, we use a form of symmetry-adapted Taylor series which we recently developed. We determine the positions of equilibrium for the ion in the presence of a continuous ring, a polygon and a polyhedron of sourses for the pair-wise forces. We also determine the states of stability for the positions of equilibrium through an examination of the second order terms in the Taylor series. We show that the general form for the Taylor series for a continuous ring is of the same form as that for a discrete polygon . We also show that small numbers of terms in the Taylor series can duplicate the exact potential for an atom within a tetrahedron or octahedron of sources to a high degree of accuracy.

Analyses for Mechanical Stability for Systems of Ions and Atoms Associated with Rings, Cages, and Crypts

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Abstract

There exist examples of systems in which small, simple metallic cations are associated with ring-like molecules (e.g., aromatic radical anions), with aggregates of molecules which encage the ion (e.g., solvation and coordination), or special molecules which trap ions within the molecular structure (crypts). For each of these examples, the harmonic oscillations of the ion in the presence of the molecular structure can be observed. Moreover, in many instances, the stability of the ionic motions in the presence of the molecular structure is important in considering some form of transport process which is associated with the ion. In this paper we present an analysis of the mechanics of the motion of an ion under the influence of various molecular structures. For our analyses, we use a form of symmetry-adapted Taylor series which we recently developed. We determine the positions of equilibrium for the ion in the presence of a continuous ring, a polygon and a polyhedron of sources for the pair-wise forces. We also determine the states of stability for the positions of equilibrium through an examination of the second order terms in the Taylor series. We show that the general form for the Taylor series for a continuous ring is of the same form as that for a discrete polygon. We also show that small numbers of terms in the Taylor series can duplicate the exact potential for an atom within a tetrahedron or octahedron of sources to a high degree of accuracy.

1. Introduction

There are many examples of systems which involve the association of an ion or atom with a ring-like molecule, with a cage-like molecule, or with an aggregate of molecules. Cation/radical anion pairs, in which the radical anion is an aromatic ring, constitute a class of examples which has been well studied.[1] In the last decade or so, considerable interest has grown around certain molecules, referred to generically as crypts, which are capable of binding small ions within a fairly rigid molecular cage.[2] Finally, the well known states of solvation or coordination of ions in solution also serve as examples.[3] For all of these systems of aggregation, it is of considerable importance to be able to specify the states of vibration and the conditions for mechanical stability for an ion or atom with respect to the larger ring, crypt, or cage of solvent or ligand. A number of transport and kinetic processes depend upon these vibrational states in order to account for part of their activation.

In this paper, therefore, we examine the vibrations and mechanical stabilities of an ion or atom which is associated with a ring, crypt, or cage of solvent. In order to carry out this examination of the vibrations and mechanical stabilities, we use a form of symmetry-adapted Taylor series which we recently developed.[4-6] An important facet of the analysis to follow builds upon the fact that polygonal rings and polyhedral cages are closely related from a mechanical point of view.

In the next section we summarize the formulae which are needed to carry out the subsequent analyses. Following that summary, we present the results of our examinations of the ring and cage systems. We examine the use of a variety of potential energy functions from the electrostatic Coulombic potential to the Buckingham exp-6 and related potentials.

We have already shown that the form of analysis summarized in the next section is very useful for the elaboration of the nature of forces which operate in solvated ionic systems.[4,7-10] These methods, we believe, also can be useful for many other applications as well.

2. The Symmetry-adapted Taylor Series

Elsewhere we have shown[5] that for a general class of functions which consist of separable and purely angular and radial parts of the form

$$G(\underset{\sim}{R}) = Y_{\lambda\mu}(\hat{R})F(R), \tag{2.1}$$

in which $Y_{\lambda\mu}(\hat{R})$ is the spherical harmonic function, the Taylor series is

$$G(\underset{\sim}{R}+\underset{\sim}{r}) = (4\pi)^{3/2} \sum_{n=0}^{\infty} \frac{r^n}{n!} \sum_{L,M,\ell,m} (-i)^{L+n} A_{n\ell} Y_{LM}(\hat{R}) Y_{\ell m}(\hat{r})$$

$$\times \left[\frac{2L+1}{(2\ell+1)(2\lambda+1)}\right]^{1/2} (L\ell 00|\lambda 0)(L\ell Mm|\lambda\mu) I_{nL}(R). \tag{2.2}$$

The vector $\underset{\sim}{r}$ is a displacement from an end-point of $\underset{\sim}{R}$. In eq (2.2) the quantity $A_{n\ell}$ is given by[11]

$$A_{n\ell} = 0 \text{ for } \ell > n \text{ and } n - \ell \text{ odd}$$

$$= \frac{(2\ell+1)n!(n-\ell+1)!!}{(n-\ell+1)!(n+\ell+1)!!} \quad \text{for } \ell \leq n \text{ and } \ell - n \text{ even} \tag{2.3}$$

The quantity $(L\ell Mm|\lambda\mu)$ is a Clebsch-Gordan coefficient[12] and $I_{nL}(R)$ is defined by

$$I_{nL}(R) = \frac{1}{(2\pi)^3}\int_0^\infty dk\ k^{n+2}\ f(k) j_L(kR) \tag{2.4}$$

in which $j_L(kR)$ is the spherical Bessel function of the first kind.[12] The function $f(k)$ defines the radial Fourier transform of $F(R)$:[5]

$$f(k) = 4\pi i^\lambda \int_0^\infty dR\ R^2 F(R) j_\lambda(kR). \tag{2.5}$$

The Taylor series for a scalar function,

$$G_0(\underset{\sim}{R}) = Y_{00}(\hat{R})[\sqrt{4\pi}F(R)]$$
$$= F(R), \tag{2.6}$$

assumes a particularly simple form:

$$G_0(\underset{\sim}{r}+\underset{\sim}{R}) = \sqrt{4\pi} \sum_{n=0}^{\infty} (r^n/n!) \sum_{\ell}(-i)^{\ell+n} A_{n\ell} P_\ell(\hat{R}\cdot\hat{r}) I_{n\ell}(R) \tag{2.7}$$

in which $P_\ell(x)$ is the Legendre polynomial[12] of order ℓ and $\hat{R}\cdot\hat{r}$ is

the scalar product of the unit vectors $\hat{R}$ and $\hat{r}$.

We have also shown[5] that the Taylor series (2.2) for a scalar function can be expressed as

$$F(\underset{\sim}{R}+\underset{\sim}{r}) = \sum_{n=0}^{\infty} (r^n/n!) \sum_{\ell} A_{n\ell} P_\ell(\hat{R}\cdot\hat{r}) \sum_{q=0}^{\ell} \frac{(-1)^q(\ell+q)!}{(\ell-q)!(2q)!!} R^{-q} \left(\frac{n-q}{R} + \frac{d}{dR}\right) (d/dR)^{n-q-1} F(R) \tag{2.8}$$

This simple form retains the angular dependencies of eq (2.2) and displays differentiations with respect only to the radial quantities.

We now list several explicit expansions of potential energy functions which we will use in the next section.

The expansion for the Coulomb potential is identical to the familiar Laplace expansion[13]

$$\frac{1}{|\underset{\sim}{R}+\underset{\sim}{r}|} = \sum_{\ell} \frac{(-r)^\ell}{R^{\ell+1}} P_\ell(\hat{R}\cdot\hat{r}). \tag{2.9}$$

For the Morse potential,

$$\phi_M(\underset{\sim}{R}) = D\exp[\alpha(R_0-R)]\{\exp[\alpha(R_0-R)] - 2\} \tag{2.10}$$

where D is the dissociation energy and α is a parameter, we have found[6]

$$\phi_M(\underset{\sim}{R}+\underset{\sim}{r}) = D \sum_{n,\ell} (-\alpha r)^n \frac{1}{n!} A_{n\ell} P_\ell(\hat{R}\cdot\hat{r}) \{2^n e^{2\alpha R_0}[2\alpha R k_{\ell-1}(2\alpha R) - (n-\ell)k_\ell(2\alpha R)] - 2e^{\alpha R_0}[\alpha R k_{\ell-1}(\alpha R) - (n-\ell)k_\ell(\alpha R)]\} \tag{2.11}$$

in which the functions $k_n(x)$ are the modified spherical Bessel functions of the third kind:[13]

$$k_n(x) = (-x)^n (x^{-1} d/dx)^n \frac{e^{-x}}{x} . \tag{2.12}$$

For an arbitrary inverse power of R, R^{-q}, we have also found[5]

$$\frac{1}{|\underset{\sim}{R}+\underset{\sim}{r}|^q} = \frac{1}{(q-2)!R^q} \sum_{n,\ell,s} A_{n\ell} P_\ell(\hat{R}\cdot\hat{r}) \frac{(\ell+s)!(q+n-s-2)!}{n!(\ell-s)!(2s)!} (-r/R)^n . \tag{2.13}$$

This expression is equivalent to one derived by Briels[14] who used functional expansions.

The Buckingham exp-6 potential

$$\phi_B(\underset{\sim}{R}) = A\, e^{-BR} - C/R^6 \tag{2.14}$$

is simply a combination of an expansion for the exponential and eq (2.13). The result is

$$\phi_B(\underset{\sim}{R}+\underset{\sim}{r}) = \sum_{n,\ell} (-r)^n \frac{1}{n!} A_{n\ell} P_\ell(\hat{R}\cdot\hat{r}) \left\{ AB^n [BRk_{\ell-1}(BR) - (n-\ell)k_\ell(BR)] \right.$$
$$\left. - \frac{1}{24} \frac{1}{R^{n+6}} \sum_{s=0}^{\ell} \frac{(\ell+s)!(n+4-s)!}{(\ell-s)!(2s)!!} \right\} . \tag{2.15}$$

It is a straightforward matter to add the Coulomb potential to any of the various forms in order to generate potential functions for ions which interact with a variety of molecular aggregates.

Crystal field calculations with the use of the Coulomb potential eq (2.9) of course are well known.[15] An essential feature of the cyrstal field calculations is the exploitation of cubic point

group symmetries to sort out various terms in the expansions. The symmetry-adapted Taylor series we have developed works similarly. The examples we investigate in the next section illustrate this.

3. Applications to Rings and Cages

We begin this section with an investigation of the system which consists of a continuous ring of matter. We develop a Taylor series for the potential energy function for such a system. Next, we examine a polygon of sources in a plane (an example of which would be the benzene ring). We show that the results obtained for the polygon bear a strikingly close similarity to those obtained for the ring. Finally, we examine systems of sources which are distributed at the vertices of a tetrahedron and an octahedron. We develop these analyses respectively from considerations of distributions of sources in triangles and squares. Additional sources are placed at appropriate positions on the axes which pass through the centres of these figures. The conditions for mechanical stability within these systems still bear some similarity to the conditions for stability which we derive for the ring and polygon.

a. Rings of source density

The classical problem of the determination of the form of the potential due to a ring of charge density is well known.[13] Similar treatments for other possible source matter densities seem not to have been given. We have considered this problem for the Yukawa (or Debye-Hückel) potential[6] and we examine it

further in this section.

We consider the general problem of the potential due to an incremental source dQ distributed continuously as a ring of matter (neutral or charged):

$$dQ = \frac{Q}{2\pi}\, d\phi_R. \tag{3.1}$$

The magnitude of R is a constant. Thus,

$$\int dQ\, P_\ell(\hat{R}\cdot\hat{r}) = \frac{Q}{2\pi}\int_0^{2\pi} d\phi_R \sum_m \frac{(\ell-m)!}{(\ell+m)!}\, P_\ell^m(\cos\theta_R)P_\ell^m(\cos\theta_r)\exp[im(\phi_R - \phi_r)]$$

$$= Q\, P_\ell(\cos\theta_R)P_\ell(\cos\theta_r). \tag{3.2}$$

The general form of the potential now is

$$G_0(\underset{\sim}{R}+\underset{\sim}{r}) = \sqrt{4\pi}Q \sum_{n=0}^{\infty} (r^n/n!)\sum_\ell (-i)^{\ell+n} A_{n\ell} P_\ell(\cos\theta_R)P_\ell(\cos\theta_r) I_{n\ell}(R). \tag{3.3}$$

The condition for equilibrium is simply

$$P_1(\cos\theta_R)I_{11}(R) = 0. \tag{3.4}$$

From this equation we identify two conditions for equilibrium:

(1)

$$P_1(\cos\theta_R) = 0, \quad \theta_R = \pi/2 \tag{3.5}$$

The position of the point of equilibrium is at the origin of $\underset{\sim}{r}$, viz.,

the centre of the ring.

The second condition for equilibrium is

(2)

$$I_{11}(R) = 0. \tag{3.6}$$

This condition may in fact be satisfied by more than one value of R. Usually, as we shall see, only one value of R is significant; the second value may correspond, for example, to the (not useful) case of infinite separation.

It is worth noting at this point that from eq (2.8)

$$I_{11}(R) = \left.\frac{dF}{dR}\right|_{R_e} = 0 \tag{3.7}$$

as one would expect.

Stability is determined, for an arbitrary form of displacement, by evaluating the second order coefficient in the Taylor series. The second order term from (3.3) is written as

$$t_2(\underset{\sim}{R}+\underset{\sim}{r}) = \sqrt{4\pi}Q\frac{r^2}{2}\left(-\frac{1}{3}I_{20}(R) + \frac{2}{3}P_2(\cos\theta_R)P_2(\cos\theta_r)I_{22}(R)\right). \tag{3.8}$$

For the first point of equilibrium, (1) above, $\theta_{R_e} = \pi/2$, $P_2(\cos\theta_{R_e})= -1/2$, and $R_e=a$, the radius of the ring, and

$$t_2^{(1)} = -\frac{\sqrt{4\pi}}{3} Q \frac{r^2}{2}\left(I_{20}(R_e) + P_2(\cos\theta_r)I_{22}(R_e)\right). \tag{3.9}$$

For an axial displacement at the centre of the ring, $P_2(\cos\theta_r) = +1$. Thus,

$$t_2^{(axial)} = - \frac{\sqrt{4\pi}}{3} Q \frac{r^2}{2} \left(I_{20}(R_e) + I_{22}(R_e) \right) \tag{3.10}$$

The sign of $I_{20} + I_{22}$ is all-important. If the sign is negative, the motion is stable.

For a transverse displacement about a position of equilibrium at the centre of the ring, $P_2(\cos\theta_r) = - 1/2$, and

$$t_2^{(trans)} = - \frac{\sqrt{4\pi}}{3} Q \frac{r^2}{2} \left(I_{20}(R_e) - \frac{1}{2} I_{22}(R_e) \right). \tag{3.11}$$

The second position of equilibrium lies on the axis which passes through the centre of the ring. At this second point, $R=R_e$ where R_e is the solution to $I_{11}(R_e) = 0$. We find,

$$\cos\theta_{R_e} = \frac{1}{R_e} [R_e^2 - a^2]^{1/2} \tag{3.12}$$

with the Legendre polynomial evaluated as

$$P_2(\cos\theta_{R_e}) = 1 - 3a^2/2R_e^2 \tag{3.13}$$

Thus,

$$t_2^{(2)} = \sqrt{4\pi} Q \frac{r^2}{2} \left(- \frac{1}{3} I_{20}(R_e) + \frac{2}{3}(1 - 3a^2/2R_e^2) P_2(\cos\theta_r) I_{22}(R_e) \right). \tag{3.14}$$

For an axial displacement, $P_2(\cos\theta_r) = +1$, and

$$t_2^{(2,axial)} = \sqrt{4\pi} Q \frac{r^2}{2} \left(- \frac{1}{3} I_{20}(R_e) + (2/3 - a^2/R_e^2) I_{22}(R_e) \right). \tag{3.15}$$

For a transverse motion, $P_2(\cos\theta_r) = -1/2$, and

$$t_2^{(2,\text{trans})} = \sqrt{4\pi}\, Q\, \frac{r^2}{2}\left[-\frac{1}{3}I_{20}(R_e) - \frac{1}{3}(1-3a^2/2R_e^2)I_{22}(R_e)\right]. \qquad (3.16)$$

It is difficult to make further progress at this point without considering specific functional forms. From the expansions of the various functions given in the last section, we are able to consider several cases.

We examine now the ring of source for the Morse potential. The equilibrium condition $I_{11}(R_e) = 0$ specifically yields

$$-2\alpha D\exp[\alpha(R_0-R_e)]\left[\exp[\alpha(R_0-R_e)]-1\right] = 0. \qquad (3.17)$$

We see that $R_e = R_0$ or $R_e = \infty$ satisfy this equation. The latter value is not useful.

The quantity R_0 in the Morse potential is a separation which is characteristic of the Morse interaction which operates between two individual, spherical masses. It is definitely the case that when the mass is distributed on a ring, positions and conditions of equilibria and stability need not conform to the conditions which apply to the simpler spherical, diatomic case. In this respect, with the use of the Morse (and other) potentials in extended distributions, we see arising conditions of interpretation which are necessary for composite potential functions such as the Stockmayer potential.[16] The Stockmayer potential is the sum of a Lennard-Jones component and a dipolar interaction. The Lennard-Jones component, operating alone, has a meaningful minimum value which is associated with a point of equilibrium for a diatomic system. When

combined with dipolar contributions, as is the case with the Stockmayer potential, the minimum of the composite function need not fall at the same place as the minimum for the Lennard-Jones component alone. Yet, typically an interpretation is given[17] which says simply that the Lennard-Jones type of minimum in a Stockmayer potential gives the location of the minimum if the dipolar component were to vanish. We see similar interpretations applying to the use of diatomic potentials for extended distributions of mass and charge.

The second order term for the expansion of the Morse potential is simply

$$\phi_{M2} = \frac{r^2}{2}\,\frac{2}{3}\alpha^2 D \exp[\alpha(R_0-R)]\Big\{2\exp[\alpha(R_0-R)](1-1/\alpha R) - 1 + 2/\alpha R + P_2(\cos\theta_r)P_2(\cos\theta_R)\Big\{4\exp[\alpha(R_0-R)](1+1/2\alpha R) - 2(1+1/\alpha R)\Big\}\Big\}. \tag{3.18}$$

The individual contributions I_{20} and I_{22} are displayed separately as

$$I_{20}^{(\text{Morse})} = -\frac{2}{\sqrt{4\pi}}\,\alpha^2 D \exp[\alpha(R_0-R)]\Big\{2\exp[\alpha(R_0-R)](1-1/\alpha R) - 1 + 2/\alpha R\Big\} \tag{3.19}$$

and

$$I_{22}^{(\mathrm{Morse})} = \frac{2}{\sqrt{4\pi}}\,\alpha^2 D\,\exp[\alpha(R_0-R)]\left\{2\,\exp[\alpha(R_0-R)]\,(1+1/2\alpha R) - 1 - 1/\alpha R\right\}. \tag{3.20}$$

Now we return to eq (3.10) and note that R=a. We have

$$I_{20}^{(\mathrm{Morse})} + I_{22}^{(\mathrm{Morse})} = -\frac{6}{\sqrt{4\pi}}\,\frac{\alpha D}{a}\,\exp[\alpha(R_0-a)]\left\{1 - \exp[\alpha(R_0-a)]\right\} \tag{3.21}$$

Thus,

$$\phi_{M2}^{(1,\mathrm{axial})} = \frac{r^2}{2}\,2\frac{\alpha D}{a}\,e^{\alpha(R_0-a)}\left\{1 - e^{\alpha(R_0-a)}\right\} \tag{3.22}$$

This quantity is greater than zero only as long as $R_0 < a$. For $R_0 > a$, motion at the centre of the ring is not stable. The mass cannot remain at the centre of the ring in this situation. It must move to a position of equilibrium elsewhere in the system.

For the transverse motion at the centre of the ring, we find

$$\phi_{M2}^{(1,\mathrm{trans})} = \frac{r^2}{2}\,2\alpha^2 D\,e^{\alpha(R_0-a)}\left\{e^{\alpha(R_0-a)}(1-1/2\alpha a) - \frac{1}{2} - \frac{1}{2\alpha a}\right\}. \tag{3.23}$$

This expression depends upon two dimensionless parameters which may be chosen from αR_0, αa, and a/R_0.

At the second position of equilibrium along the axis of the ring, we find for eq (3.15)

$$\phi_{M2}^{(2,axial)} = \frac{r^2}{2} \; 2\alpha^2 D(1 - a^2/R_0^2) \tag{3.24}$$

and for eq (3.16)

$$\phi_{M2}^{(2,trans)} = \frac{r^2}{2} \; 2\alpha^2 D \; \frac{a^2}{R_0^2} \; . \tag{3.25}$$

Each of these motions is stable. Indeed, for $a^2/R_0^2 = 2/3$, the resultant harmonic potential is spherical. This particular point lies at an altitude $h = 0.71a$ above the plane of the ring.

For the Buckingham exp-6 potential, the situation is more complicated. Because the potential, as we have listed it, does not depend on a diatomic equilibrium separation R_0, it is not as simple here to identify the condition for instability at the centre of the ring or elsewhere.

The radial equilibrium condition $I_{11}(R_e) = 0$ is found to be

$$ABe^{-BR_e} - 6C/R_e^7 = 0. \tag{3.26}$$

The general second order term is

$$\phi_{B2} = \frac{r^2}{2} \; \frac{1}{3}\Big[AB^2(1-2/BR)e^{-BR} - 30C/R^8 + 2P_2(\cos\theta_R)P_2(\cos\theta_r)$$

$$\times\left(AB^2(1-1/BR)e^{-BR} - 48C/R^8\right)\Big] \tag{3.27}$$

Again, for the consideration of equilibrium at thecentre of the ring, R=a. For the axial displacement,

$$\phi_{B2}^{(1,axial)} = \frac{r^2}{2}\,\frac{1}{3}\left(-\frac{AB}{a}e^{-aB} + 18\frac{C}{a^8}\right). \tag{3.28}$$

Here we find that if

$$AB\,e^{-aB} > 18C/a^7,$$

the axial displacement at the centre of the ring will be unstable.

For the transverse displacement, we find

$$\phi_{B2}^{(1,trans)} = \frac{r^2}{2}\,\frac{1}{3}\left(\frac{1}{2}AB^2(3-5/aB)e^{-aB} - 54C/a^8\right). \tag{3.29}$$

For the second position of equilibrium, outside the ring, but along the axis, we find

$$\phi_{B2}^{2} = \frac{r^2}{2}\,\frac{1}{3}AB^2e^{-BR_e}\left((1-7/BR_e) + 2(1-9/BR_e)P_2(\cos\theta_r)P_2(\cos\theta_{R_e})\right) \tag{3.30}$$

where we have used eq. (3.26) to eliminate C/R_e^8 terms. For an axial displacement, we find

$$\phi_{B2}^{(2,axial)} = \frac{r^2}{2}\,\frac{1}{3}AB^2e^{-BR_e}\left(3 - \frac{25}{BR_e} - 3\,\frac{a^2}{R_e^2}(1+9/BR_e)\right). \tag{3.31}$$

For the transverse displacement, we find

$$\phi_{B2}^{(2,trans)} = \frac{r^2}{2}\,\frac{1}{3}AB^2e^{-BR_e}\left(\frac{3a^2}{2R_e^2}(1+9/BR_e) - 2/BR_e\right). \tag{3.32}$$

In these cases, it is necessary to test numerically for equilibrium with the use of specific values of the quantities A, B, and C.

If the Coulomb potential is added for a charged system, it is necessary to add terms of the form

$$\phi_C(\underset{\sim}{R}+\underset{\sim}{r}) = q\sum_{\ell} P_\ell(\cos\theta_R)P_\ell(\cos\theta_r)\frac{r_<^\ell}{r_>^{\ell+1}} \tag{3.33}$$

in which $r_{<(>)}$ is the lesser (greater) of R and r. The addition of terms to the potential clearly makes the task of finding stabilities more difficult. However, the formalism does allow one to proceed directly to answer such questions as those pertaining to stability.

b. Polygonal distributions of discrete sources

We write the general expansion of an arbitrary scalar function for a collection of sources as

$$G_0(\underset{\sim}{R}+\underset{\sim}{r}) = \sqrt{4\pi}\sum_{n=0}^{\infty}(r^n/n!)\sum_{\ell}(-i)^{\ell+n}A_{n\ell}\sum_{I}P_\ell(\hat{R}_I\cdot\hat{r})I_{n\ell}(R_I) \tag{3.34}$$

where the summation over I is considered over sources. For a regular polygon, all R_I are the same, R. The angular distributions with respect to the centre of gravity of the distribution, of course, differ. Consider, therefore, the sum over unit vectors $\hat{R}_I$:

$$\begin{aligned}\sum_I P_\ell(\hat{R}_I\cdot\hat{r}) &= \frac{4\pi}{2\ell+1}\sum_{m=-\ell}^{\ell}Y^*_{\ell m}(\hat{r})\sum_I Y_{\ell m}(\hat{R}_I)\\ &= \sum_m \frac{(\ell-m)!}{(\ell+m)!}P_\ell^m(\cos\theta_r)P^m(\cos\theta_R)e^{-im\phi_r}\sum_I e^{im\phi_{R_I}}\end{aligned} \tag{3.35}$$

For a regular polygon, $\phi_{R_I} = 2\pi n/N$, where N is the total number of discrete sources, and n = 0,1,2,...,N-1. Thus,

$$\sum_{n=0}^{N-1} \exp(i2\pi mn/N) = N\delta_{m,0}. \tag{3.36}$$

Hence,

$$G_0(\underset{\sim}{r}) = \sqrt{4\pi}\, N \sum_{n=0}^{\infty} (r^n/n!) \sum_{\ell} (-i)^{\ell+n} A_{n\ell} P_\ell(\cos\theta_R) P_\ell(\cos\theta_r) I_{n\ell}(R) \tag{3.37}$$

where each θ_R is the same for a plane of sources.

Eq (3.37), apart from the number of discrete sources N, is exactly the same as (3.3). Hence, all conditions of stability fournd for the continuous ring apply equally to the regular polygonal distribution of sources.

c. Cages of sources: regular polyhedra

We now consider regular polyhedral cages of sources. These cages are constructed easily by distributing sources at the vertices of tetrahedrons, octahedrons, etc. The tetrahedron, for example, can be realized in terms of a base triangle with a fourth source located at an appropriate position on the axis which passes through the centre of the triangle. An octahedron is realized similarly. The plane of sources defines a square. Two additional sources are placed axially.

In order to investigate the stabilities of these systems, we make use of the expressions for t_2 for polygons together with as many additional terms for the axially located sources as needed. In the following, we consider the tetrahedron and octahedron as the most typically encountered examples. More complicated systems easily are generated.

Considering first the tetrahedron, we construct a base triangle of sources. *In order to examine the mechanical stability of a test* particle located at the origin of the tetrahedron, we consider a point above the plane. Thus,

$$t^{(2)}_{2T(a)} = \sqrt{4\pi}\,\frac{r^2}{2}\left[-I_{20}(R) + 2(1-3a^2/2R^2)P_2(\cos\theta_r)I_{22}(R)\right]. \qquad (3.38)$$

We locate the fourth source on the z-axis at a distance R from the centre of the tetrahedral origin. Thus,

$$t_{2T(b)} = \sqrt{4\pi}\,\frac{r^2}{2}\left[-\frac{1}{3}I_{20}(R) + \frac{2}{3}P_2(\cos\theta_r)I_{22}(R)\right]. \qquad (3.39)$$

The sum of these two terms gives

$$t_{2T} = \sqrt{4\pi}\,\frac{r^2}{2}\left[-\frac{4}{3}I_{20}(R) + \frac{2}{3}(4-9a^2/2R^2)P_2(\cos\theta_r)I_{22}(R)\right]. \qquad (3.40)$$

If, for example, we consider the locations of the sources on the triangle to be $(0, 2\sqrt{2}R/3, -R/3)$ and $(\pm\sqrt{2/3}R, -\sqrt{2}R/3, -R/3)$, then it is easy to see that $a^2/R^2 = 8/9$. Hence,

$$t_{2T} = \sqrt{4\pi}\,\frac{r^2}{2}\left[-\frac{4}{3}I_{20}(R)\right]. \qquad (3.41)$$

For the octahedron, on the other hand, the base plane of (4) sources contains the centrum of the system. Thus, we consider the expression

$$t^{(1)}_{2O(a)} = \sqrt{4\pi}\,\frac{r^2}{2}\left[-\frac{4}{3}I_{20}(R) - \frac{4}{3}P_2(\cos\theta_r)I_{22}(R)\right] \qquad (3.42)$$

for displacements about the centre. A second term for the additional two axial sources is

$$t_{20(b)} = \sqrt{4\pi}\,\frac{r^2}{2}\left(-\frac{2}{3}I_{20}(R) + \frac{4}{3}P_2(\cos\theta_r)I_{22}(R)\right). \tag{3.43}$$

The sum is

$$t_{20} = \sqrt{4\pi}\,\frac{r^2}{2}\left(-2I_{20}(R)\right). \tag{3.44}$$

In both the cases of the tetrahedron and octahedron, the second order Legendre polynomial disappears as is required by arguments of symmetry.

It is useful now to investigate these results with the use of specific functional forms. The use of the Morse potential yields physically transparent and interesting conditions for stability. For the Morse potential, for example, we can write

$$\phi_{2M(T)} = \frac{r^2}{2}\,\frac{8}{3}\alpha^2 D\,\exp[\alpha(R_0-R)]\Big\{2\,\exp[\alpha(R_0-R)](1-1/\alpha R) - 1 + 2/\alpha R\Big\}. \tag{3.45}$$

If $R = R_0$, the force constant for an encaged particle is

$$k_T = \frac{8}{3}\alpha^2 D, \tag{3.46}$$

a result which we have found elsewhere.[4] Similarly, the force constant for the displacement of a test particle about the centre of an octahedron of sources is

$$k_0 = 4\alpha^2 D. \tag{3.47}$$

In both of these cases, it is clear that the motions are mechanically stable.

It is possible to consider the general question of the stability of displacements about the centre of gravity and symmetry in these structures. From eq (3.19) we note that when

$$2\exp[\alpha(R_0-R)](1-1/\alpha R) - 1 + 2/\alpha R < 0, \tag{3.48}$$

a displacement is mechanically unstable. The condition (3.48)--for the Morse potential--reduces easily to the following inequality:

$$R > R_0 + \frac{1}{\alpha}\ell n 2. \tag{3.49}$$

When this inequality is satisfied, instability is guaranteed.

Such conditions of instability may be observed in actual systems. Weaver (personal communication) has observed that the attempted reduction of lithium 2.1.1 cryptate to form the encrypted atom is electrochemically irreversible. The gross difference in size of the atom as compared to the cation suggests the system may be unable to accomodate the atomic species. If the encrypted species is mechanically unstable in that location, then some form of tunnelling out of the crypt would be expected rapidly to occur.

d. A truncated Taylor series versus the exact potential: a comparison

We conclude this section by comparing a truncated Taylor series for the Morse potential against the potential itself. We consider again the tetrahedral cage of sources, each of which is described by the Morse potential.

The choice for the origin of the Taylor series is the point of equilibrium at the centre of the tetrahedron. The four vectors $\underset{\sim}{R}_i$ $(1 \leq i \leq 4)$ from the centres of force to that point have the same length R. Thus, only the angular factors differ in the four individual Taylor series. The superposition of the Taylor series requires the consideration of

$$\sum_{i=1}^{4} P_\ell(\hat{R}_i \cdot \hat{r}) \tag{3.50}$$

in the manner previously discussed [cf., the last subsection]. This resultant angular factor can be evaluated for arbitrary directions of r. This angular factor (3.50) vanishes for $\ell = 1$ because we have chosen the point of equilibrium to be the origin. It also vanishes for $\ell = 2$ because the system has no quadrupole symmetry. We were surprised to discover that it also vanishes for $\ell = 5$, although it does not vanish for any other value of ℓ up to 12.

In order to demonstrate the non-spherical nature of the resultant potential, we have chosen three particular directions for r. One of these is toward a vertex of the tetrahedron, i.e., directly toward one of the centres of force. Another is toward the midpoint of a face of the tetrahedron, i.e., directly away from one of the

centres of force. One can anticipate that these should be respectively the directions of the most rapid and least rapid increase of potential. The third direction was chosen toward the midpoint of an edge of the tetrahedron, and should represent any intermediate rate of increase of the potential. The exact expression for the resultant potential can also be readily evaluated along these directions.

In Figure 2 we show the result of an evaluation for the particular choice of parameters $\alpha R = 4$ and $\alpha R_0 = 6$. We note the following particular features which are revealed in the figure. (1) The potential is spherical and harmonic at the centre. (2) The aspherical and anharmonic contribution is well described by n=3, ℓ=3 out to about r=0.1R (one third of the way to the face). (3) The resultant potential is extremely well described by terms up to n=6.

Similar results are obtained for an octahedron of centres of force. In this case, however, the resultant potential exhibits an even more spherical character. The exact potential is effectively duplicated with the use of terms n=2,4,6. For the tetrahedron, in contrast, n=2,3,4,5,6; i.e., five terms are needed to give a good fit. In both cases the actual potential functions are well represented by a small number of terms.

4. Summary and conclusions

We have used a symmetry-adapted form of the Taylor series in order to investigate the nature of the stabilities predicted for several mechanical systems. In particular, we have examined rings, polygons, and polyhedra all of which share similar mathematical properties.

The examination of the system of a continuous circular distribution of matter which interacts with a point mass showed two fundamental positions of equilibrium: one is at the centre of the ring and the other is on the axis. We established the conditions for the points of equilibrium to be stable. Next, we showed that a regular polygon is mathematically similar to the continuous ring. The conditions for equilibrium and stability are the same for both systems. Finally, we showed that questions of stability could be answered for regular polyhedra by making use of the results for the polygons. It is possible to show, for the cases of the tetrahedron and octahedron, that under certain conditions even an enclosed point of equilibrium at the centre of a regular solid can exhibit a mechanical instability with respect to displacements about that point.

We believe these results to be generally useful for a number of applications. The point of view which we adopt in carrying out our analyses is that one mass be examined with reference to the static collection of surrounding masses (sources of force). For a number of systems, it is sufficient merely to focus attention on a single particle, such as a solvated ion. When this limited view is too restrictive, it is quite simple successively to look at each mass in a collection of interacting masses and develop a succession of Taylor series. Thus, in this manner the realistic harmonic vibrational force field can be developed for a system such as a molecule. The subsequent development is a picture which is familiar as vibrational spectroscopy. For scalar potentials, the use of our form of the Taylor series enables one quickly to calculate harmonic and higher order contributions.

The analyses of mechanical stability for polygons and polyhedra

are important in the consideration of several transport processes. The surface of a metal or semiconductor, for example, at which electrochemical oxidation or reduction can take place can be viewed accurately as an extended surface network of interconnected polygons. Thus, the question of the stability of a particle which interacts with several polygons is important in the determination of the process of surface migration. Simple systems, such as these extended polygons as surfaces in vacua, can be rendered more complex by considering additional distributions of molecules about the surface. The question of the stability of a single particle enmeshed in such a complex is still a resolvable question. The system can be modelled. Positions of equilibrium can be established easily. And, finally, stability against displacement for a particle can be determined. All of this can be done for a wide variety of model potential energy functions. As an example, in a separate paper, we consider the relative stabilities of solvated ions and atoms, and the implications these stabilities have on the deposition of a metal atom at an electrode surface.[8]

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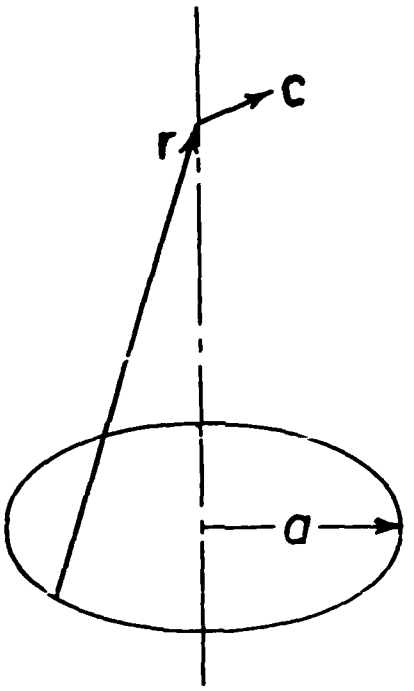
Figure captions:

Figure 1. The geometry for the determination of the equilibrium condition near a ring of source for the Morse potential.

Figure 2. The potential energy as a function of displacement along the radii in a tetrahedral cage of sources for the Morse potential. As indicated in the inset, the radii are directed toward a vertex (V), toward a face (F), or toward an edge (E). The maximum displacement considered is one-third of the distance to a vertex, i.e., the distance to a face. The dashed curve in each labelled pair is produced by the Taylor series to order r^3, while the solid curve represents (within the width of the line) both the exact superpotision of the Morse potentials and the Taylor series to order r^6.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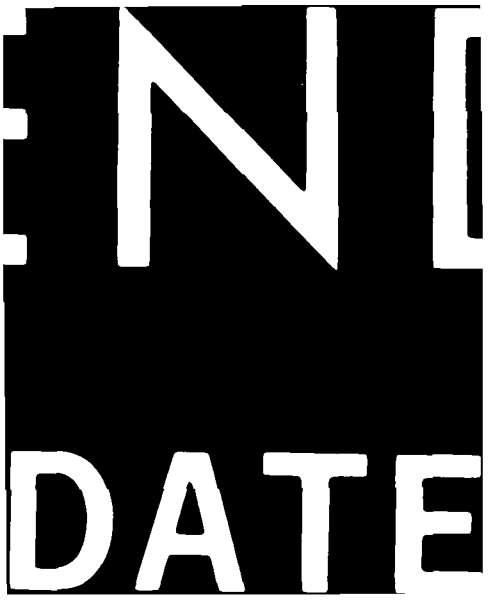
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